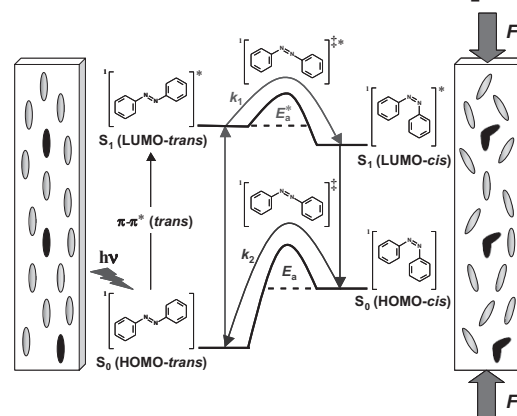


Opto-Mechanical Effect in Photoactive Nematic Side-Chain Liquid-Crystalline Elastomers^a

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The mechanical behaviour of monodomain nematic side-chain liquid-crystalline elastomers containing azoderivatives as pendant groups or crosslinkers has been studied under UV irradiation and in the darkness at different temperatures. From the evaluation of the opto-mechanical experiments, the mechanical efficiency, kinetic rates, activation energies and the isomerization mechanism of the azocompounds in the liquid-crystalline matrix could be determined, as well as the effect of the chemical constitution of the azobenzene derivatives and their role in the elastomeric network.



Introduction

Nematic liquid-crystalline elastomers (LCEs) combine the internal coupling of liquid-crystalline order and the chain configuration of a polymer network.^[1] If the system is microscopically ordered this order is related to its macroscopic dimensions.^[2,3] The molecular structure of a side-chain liquid-crystalline elastomer (SCLCE) is similar to that of conventional rubber, as it consists of long chains of molecules that can slide past each other easily and thus allow the material to be stretched with little effort. Attached to these chains there are smaller rod-like molecules that are usually found in liquid crystals (LC).^[4–6] When some

photosensitive molecules are attached as pendant or crosslinker units, the material can interact with light and can misalign the long chains and give unexpected mechanical properties, such as the ability to drastically change its shape up to 60% either when it is heated or when light falls on it.^[7–10] Such materials have a variety of potential uses, as switches, actuators, or artificial muscles (sensor or movement actuator).^[11–17]

We are interested in investigating the response of nematic SCLCEs that contain azoderivatives^[18,19] as pendant co-monomers^[9,20] or crosslinkers^[7,10] in order to establish the effect of their architecture when an external field (heat or light) is applied. Under irradiation, the change in shape of these azoderivatives, from the rod-like shape (*trans*-isomer) to the bended-like shape (*cis*-isomer), leads to a local disorder in the sample that is related to a change in the dimensions of the elastomer.

Studies were done on LCEs doped with low molecular-mass photosensitive dyes.^[10,21] Their macroscopic response was studied, showing some local heating-induced disorder actuation (thermal effect). All these systems showed low mechanical actuation because of the non-covalent attachment of the dye to the polymer backbone. It was our intention to study and isolate only the photo-isomerization

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(photochemical process) and the thermal back-isomerization, as well as to enhance the response by attaching the azobenzene molecules to the network as pendant molecules of crosslinkers.

In this paper we show new opto-mechanical results of photoactive LCEs and the effect of the chemical constitution of the azoderivatives, together with their role in the elastomeric network: mechanical and/or disorder-induced effects due to the architecture of the pendant or crosslinker azoderivatives.

Experimental Part

Synthesis of the Mesogen, Crosslinker and Azobenzene Derivatives

Two series of azobenzene derivatives were synthesized in order to assess the effect of the co-monomers as pendant group (p) or as crosslinker (c) in a liquid-crystalline matrix. The first series contained the pendant and the crosslinker azoderivative made of two aromatic rings (Azo2-p and Azo2-c); the second one contained four aromatic rings (Azo4-p and Azo4-c) (see insets in Figure 3). The 4-hydroxy-4'-methoxyazobenzene (MHAB) was synthesized according to literature,^[22] and the 4,4'-dihydroxyazobenzene (DHAB) by demethylation of the MHAB with BBr_3 in CH_2Cl_2 .^[23] Three completely new azoderivatives were synthesized: Azo2-c, Azo4-p, and Azo4-c. All synthetic steps are described in the Supporting Information (Scheme SI-1). The rod-like mesogen (MPBB) and the isotropic crosslinker (SCC) were synthesized as described in previous papers.^[4–6,24]

Synthesis of Photoactive Nematic Side-Chain Liquid-Crystalline Elastomers

The orientated nematic LCEs were prepared using the spin-casting technique.^[24] After the non-complete hydrosilylation reaction,^[25–28] the samples were removed from the reactor and aligned by applying a uniaxial stress. The curing process allowed finishing the hydrosilylation reaction, and keeping the alignment of these samples – second step crosslinking reaction in the nematic phase during the orientation of the samples. The composition of these samples was optimized at a level of azobenzene dyes high enough to see the opto-mechanical effect of the azoderivatives as pendant groups or crosslinkers, but not that high that full absorption of light could happen in the first single layers of the sample. All four samples were synthesized using the same quantity of olefins which are related to all crosslinker units: 20 mol-% of crosslinking double bonds (11.1 mol-% of crosslinker). The quantity of azoderivative was always constant: only 5.6 mol-% of azounits, due to the high absorption of these chromophors (see Supporting Information, Scheme SI-2). For this crosslinking composition, all samples have 16 side-chain repeating units between two crosslinkers, and for the samples with the azocompound as pendant group this photo-switchable molecule represents 1 out of the 16 units.

X-ray measurements showed that these nematic samples were well oriented and with values of the order parameter from 0.74 to

0.77 and distances in between mesogenic units of 4.4 to 4.5 Å. The presence of azomolecules clearly determines the mechanical and thermal properties of the samples. A sample with the same crosslinking density but with no azoderivative was synthesized, in order to compare the effects of the guest azomolecules. This non-photoactive elastomer showed a clearing temperature of 68 °C while the four photoactive elastomers have clearing temperatures from 70 to 107 °C (see Supporting Information).

Apparatus and Techniques

Opto-mechanical measurements were performed with a self-constructed apparatus designed to measure the retroactive force as function of time under irradiation, or the relaxation process in the darkness (see Supporting Information, Figure SI-1). In a thermostated cell controlled by a Haake-F6 thermostat and a Pt100 thermoresistor, the sample was stretched by one Owis SM400 microstep motor and controlled by an Owis LSTEP-12 56.202.0000 microstep controller. The stress (σ) was measured by a Transducer Techniques GS0-10 transducer load cell (10 g) and analysed by a Newport Electronics INFS-1001-DC7 high performance strain gage indicator. All relevant data such as temperature, time and stress (σ) were continuously logged and controlled by National Instruments LabView 7.0 software. The sample was irradiated with UV-light using a Osram XBO150 W/1 xenon arc lamp (150 W, 20 V, 7.5 A) that was in a Müller Elektronik-Optik LAX 1530 lamp housing connected to a Müller Elektronik-Optik SVX 1530 power source. To select the right wavelength, a Jobin Yvon H20 UV/Vis/NIR monochromator was used and a Ocean Optics USB2000 UV-Vis spectrophotometer (UV2/OFLV-4 detector, L2 lens, 5 μm slit, 200–850 nm) connected to the thermostated cell by a Ocean Optics P400-2-UV/VIS optical fibre (UV-Vis, 2 m, 400 μm) was attached to the back side of the cell. The temperature of the sample was checked by using a Eurotherm Controls 2132 PID temperature controller with a 4–20 mA linear thermocouple type Pt100 attached to a parallel piece of the sample. The intensity of the radiation reaching the sample was 312 $\text{mW} \cdot \text{cm}^{-2}$, measured by a calibrated Lot-Oriel Ophir-70260-2 radiant power meter with a Lot-Oriel Ophir-70282 Si-detector with PD300-UV head in the range from 250 to 1100 nm, and it was kept constant during the experiments.

Results and Discussion

Opto-Mechanical Experiments

We investigated the response under irradiation of nematic photoactive SCLCEs which contain azobenzene derivatives as pendant co-monomers or as crosslinkers with the aim to establish the effect of their chemical constitution (connectivity and dimensions of the azo dyes) when an external field – light in this case – is applied.

Photo-isomerizable rod-like molecules undergo a molecular transition from the *trans* to the *cis* state on absorbing an appropriate photon. They strongly bend and no longer contribute to the liquid-crystalline ordering, in fact they act as an impurity and destabilize the order.^[29] One might then

expect UV illumination to induce contractions in LCEs containing such molecules analogous to those observed thermally.^[7–10] This effect could be induced by the fact that the *cis*-isomer is a kind of impurity in the liquid-crystalline order, and by the mechanical stress generated by the azobenzene crosslinkers.

We studied and isolated the photochemical process (photo-isomerization) and the back-isomerization (thermal-isomerization). In order to investigate the opto-mechanical effect of these photoactive elastomers, a new set-up with the option of choosing different wavelengths was built where all thermal effect is removed and only photo-isomerization effect is measured. With this set-up the mechanical stress (σ) under irradiation can be measured as function of time and temperature.

In a LCE with azobenzene derivatives, when the azobenzene compound is isomerized (from *trans* to *cis*) the local order parameter (S) and the nematic-to-isotropic phase transformation temperature (T_{NI}) decrease, causing a microscopic local disorder in the mesogens and a consequent change in the macroscopic length of the sample (Figure 1). Then, a big change in the macroscopic dimensions (λ) can be predicted in the vicinity of the T_{NI} due to the photo-isomerization process.

If the experiment is carried out at one temperature below the clearing temperature for both isomers (*cis*- T_{NI} and *trans*- T_{NI}), the photo-isomerization of the azobenzene compound causes a small decrease in the order parameter, and consequently a small change in length (from point *a* to *b* in Figure 1). When the experiment takes place between both clearing temperatures, a dramatic change in the order parameter is caused by the illumination of the sample, and a big change in the dimensions of LCE sample can be observed (from point *c* to *d* in Figure 1).^[8] Thus, every negative change in length should induce an increase in the stress when the sample is fixed from both extremes.

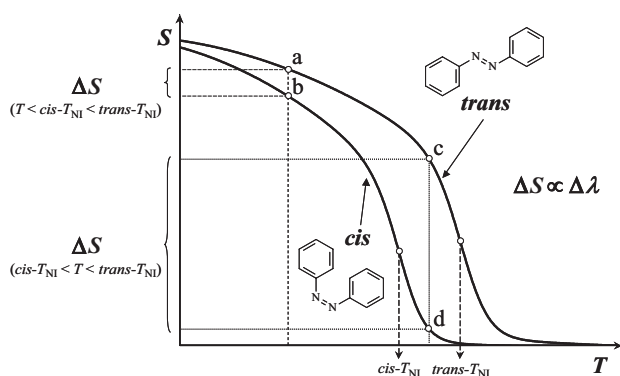


Figure 1. Order parameter (S) as function of temperature for a LCE containing azobenzene molecules. The *trans*-isomer stabilizes the liquid-crystalline phase and has higher clearing temperature (*trans*- T_{NI}), while the *cis*-isomer destabilizes the liquid-crystalline phase, reducing the local order, and shifting the clearing temperature to lower values (*cis*- T_{NI}).

The rate for the population of molecules for the forward *trans*-to-*cis* (photo-isomerization) reaction depends on the rate delivery of photons to the azo-bonds. The *cis*-to-*trans* back reaction can be spontaneous, that is thermally (thermal-isomerization) activated in the dark, or stimulated by illumination by light (photo-back-isomerization). If these photoactive LCEs are clamped, irradiation generates a retractive force, because when the natural length diminishes, the fixed actual length is equivalent to the stress generated by elongation.

Photo-Isomerization, Thermal-Isomerization and Photo-Stationary State

In a photoactive LCE with azobenzene derivatives, the change of the local order parameter (S) depends on the ratio between the isomers from the azobenzene compound. Thus, when the azobenzene compound is isomerized (from *trans*-isomer to *cis*-isomer), the local order parameter and the T_{NI} decrease.

The opto-mechanical response of SCLCE is investigated under constant pre-load of the sample. When irradiated with UV-light ($\lambda = 380$ nm for samples SCEAzo2-p-10 and SCEAzo2-c-10, and $\lambda = 360$ nm for samples SCEAzo4-p-10 and SCEAzo4-c-10), the *trans*-*cis* isomerization causes a decrease of the local order parameter, which could be measured by an increase of the retractive force. The wavelength for irradiation was chosen based on the maximum mechanical response, as measured for each dye and from their UV-Vis absorption spectrum (see the characterization of the SCLCEs in the Supporting Information). From these measurements, the kinetics of the isomerization process can be easily evaluated.

The common procedure for opto-mechanical experiments consists of fixing the sample (10 mm \times 1 mm \times 0.3 mm) at both extremities of the longest dimension along the director. One of the extremities of the sample is attached to the load cell, measuring the retractive force on irradiating, and the relaxation process when stopping to irradiate. After reaching the set temperature, a pre-load (0.5 g which corresponds to a strain of $\lambda = 1.01$) was applied to the sample to get it well oriented and straight, and the irradiation process started. Because the sample cannot shrink, a retractive force appears. This force is measured as function of time until reaching the photo-stationary *cis*-*trans* equilibrium. On arriving to this steady state, the sample was not irradiated anymore and a relaxation process started.

During the irradiation process, not only the *trans*-*cis* photo-isomerization is present. The *cis*-*trans* thermal-isomerization is also there at all times, and when the photo-stationary state is reached both are in dynamic equilibrium. Thus, the curve describing the photoactivation process (k_{photo}) is an exponential growth (Equation 1)

with a lifetime that is related to both the photo-isomerization (k_1) and the thermal-isomerization (k_2) processes, $\tau_{\text{photo}} = (k_1 + k_2)^{-1} = k_{\text{photo}}^{-1}$. On introducing an exponential factor (β_{photo}) in Equation 1, one can analyse whether the data from opto-mechanical experiments fit with the ideal case of a simple exponential function ($\beta_{\text{photo}} = 1$). The stretched exponential function takes in consideration the pre-load applied ($\Delta\sigma_0$) to the sample, the maximum mechanical response ($\Delta\sigma_{\text{max}}$), as well as any deviation from the simple exponential function.

$$\Delta\sigma = \Delta\sigma_{\text{max}} \left(1 - \exp\left(\frac{-(t-t_0)}{\tau_{\text{photo}}}\right)^{\beta_{\text{photo}}}\right) + \Delta\sigma_0 \quad (1)$$

When switching the light off, only the thermal-isomerization process takes place (the *cis*-isomer transforms to the *trans*-isomer) and the mechanical stress vanishes. The equation that describes this thermal process (k_{thermal}) is an exponential decay (Equation 2) with a lifetime that is related only to the thermal-isomerization (k_2) process, $\tau_{\text{thermal}} = (k_2)^{-1} = k_{\text{thermal}}^{-1}$. Similarly to the photo-isomerization process, an exponential factor (β_{thermal}) was introduced to this exponential decay in order to evaluate the deviation of the experimental points with respect to the ideal case ($\beta_{\text{thermal}} = 1$). The resulting stretched exponential decay considers the pre-load applied initially ($\Delta\sigma_0$) to the sample, the starting maximum mechanical response ($\Delta\sigma_{\text{max}}$), and the deviation from simple exponential decay.

$$\Delta\sigma = \Delta\sigma_{\text{max}} \exp\left(\frac{-(t-t_0)}{\tau_{\text{thermal}}}\right)^{\beta_{\text{thermal}}} + \Delta\sigma_0 \quad (2)$$

First experiments (Figure 2a) were done using a filter that removes the entire visible spectrum but not some infrared wavelengths. Two effects in the mechanical response of the sample could be observed. When the

sample is in the darkness, after irradiation, the fast process corresponds to the thermal effect, which takes place until the sample reaches thermal equilibrium with the block system. That means a decrease in the temperature of the sample that relaxes. The second process is the *cis-trans* thermal-isomerization, which happens along all the relaxation process. In the same manner, during the irradiation of the sample these two processes can be differentiated: the fast thermal effect, which raises the temperature of the sample – trying to contract the sample and generating extra stress-, and the *trans-cis* photo-isomerization, which is in balance to the *cis-trans* thermal-isomerization upon reaching the photo-stationary equilibrium state.

In the irradiation process the quality of the light used can affect the response. One should remove all wavelengths that are not needed (visible light and infrared irradiation) in order to avoid any extra stress. For this reason one can use (i) a combination of filters (UV-transmitting filter and an IR-cut-off filter) or (ii) a monochromator in order to irradiate at the precise absorption wavelength of the dye.

Opto-Mechanical Response

Opto-mechanical experiments on a sample of a SCLCE with azobenzene derivative as crosslinker showed the behaviour of the stress ($\Delta\sigma$) as function of time presented in Figure 2b. When the sample was irradiated with UV-light, an exponential growth of the stress towards a photo-stationary equilibrium state was observed. Turning off the irradiation, the reverse process occurred.

While the *trans-cis* process can be accelerated with the intensity of the UV radiation or the substitution in the azobenzene molecule (push-pull systems),^[30] the thermal-back-reaction depends only on the chemical constitution of the azobenzene compound. The opto-mechanical experi-

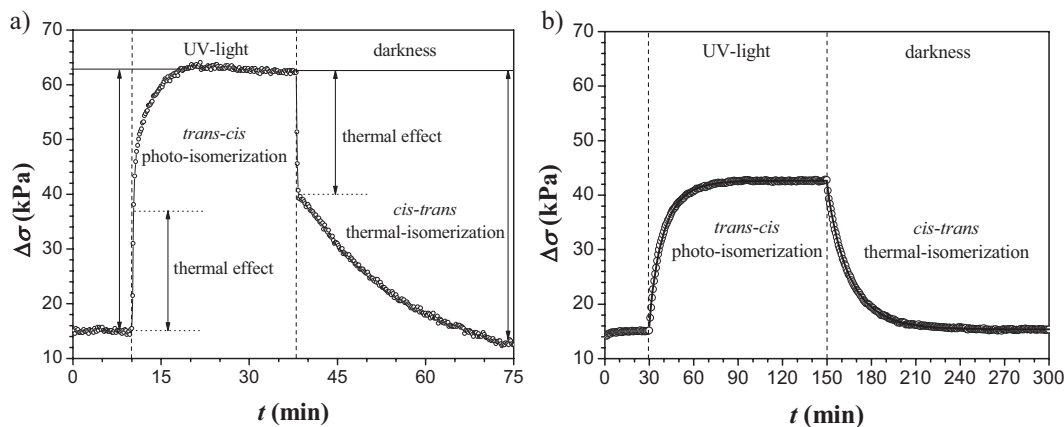


Figure 2. Opto-mechanical experiments on the SCEAz02-c-10 at 50 °C a) with IR unfiltered light, and b) with monochromatic light at $\lambda = 380$ nm (the curves are the best fits to both processes).

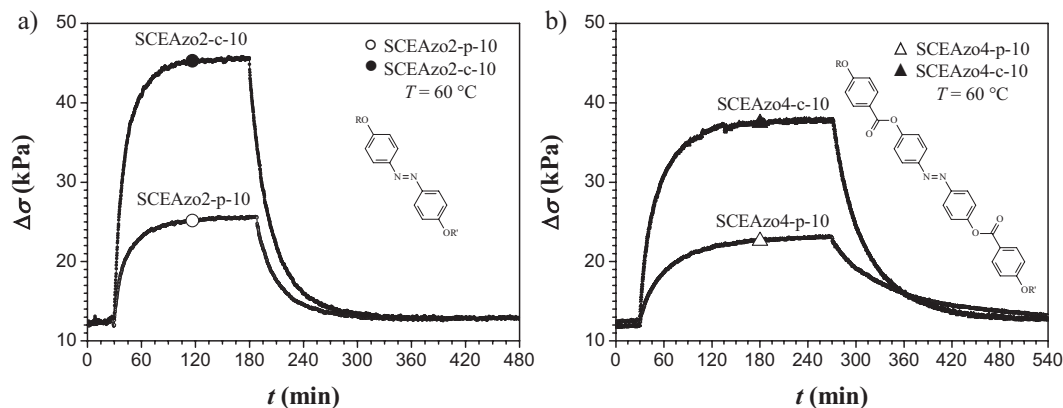


Figure 3. Opto-mechanical experiment at 60 °C on the samples a) SCEAzo2-p-10 ($R = \text{CH}_3$, $R' = (\text{CH}_2)_4\text{CH} = \text{CH}_2$) and SCEAzo2-c-10 ($R = R' = (\text{CH}_2)_4\text{CH} = \text{CH}_2$) at $\lambda = 380$ nm), and b) SCEAzo4-p-10 ($R = \text{CH}_3$, $R' = (\text{CH}_2)_4\text{CH} = \text{CH}_2$) and SCEAzo4-c-10 ($R = R' = (\text{CH}_2)_4\text{CH} = \text{CH}_2$) at $\lambda = 360$ nm.

ments have been performed at different temperatures to identify the activation energy of the photo- and back-isomerization processes.

This process is monitored by measuring the force that appears when the elastomer tries to shorten but it is physically blocked. In Figure 3, opto-mechanical experiments are shown where the two isomerization processes are presented for all four photoactive SCLCEs. Each curve contains the equilibrium between photo- and thermal-isomerization (first part of the curves) and the pure thermal-isomerization (second part of the curves).

From the opto-mechanical curves on SCLCEs at the same temperature (Figure 3), two effects can be observed due to chemical constitution and connectivity. First, azobenzene molecules as crosslinkers show a mechanical response from 2.2 to 2.5 times higher in average with respect to the corresponding pendant azobenzene groups at the same temperature. Their light induced stress is 60% due to the crosslinker nature, and 40% due to *cis*-isomer disorder induced shape. Second, azobenzene molecules with two aromatic rings are more efficient (25% for pendant groups and 12% for crosslinkers) than four aromatic rings

molecules in terms of opto-mechanical response due to their rigidity.

Performing the same experiment at different temperatures one can calculate the maximum stress ($\Delta\sigma_{\text{max}}$), kinetics constants (k_1 and k_2) and the exponential factors (β_{photo} and β_{thermal}) for both processes. The values of these exponential factors (Table 1) place the samples' behaviour extremely close to pure simple exponential growth ($\beta_{\text{photo}} \approx 0.71\text{--}0.83$) or decay ($\beta_{\text{photo}} \approx 0.82\text{--}0.90$).

When plotting the maximum opto-mechanical response ($\Delta\sigma_{\text{max}}$) as function of temperature, it appears again that SCLCEs with azobenzene crosslinkers are more efficient than pendant groups. The most efficient SCLCE system is the one having two aromatic rings, composed of the azobenzene molecule as a crosslinker (Figure 4).

We believe that the high mechanical efficiency of this azobenzene compound (Azo2-c) is due to its more restricted movements, compared to the four aromatic rings azobenzene compound (free movements from the two esters groups). The azobenzene crosslinkers are not only inducing disorder due to the changing in molecular shape from *trans* to *cis*. They create an extra mechanical

Table 1. Exponential factors during the photo-isomerization (β_{photo}), and the thermal-isomerization (β_{thermal}) processes, and their corresponding activation energies (E_a) and half-life times ($t_{1/2}$) at 50 °C for each sample

Sample	Photo-isomerization			Thermal-isomerization		
	β_{photo}	E_a	$t_{1/2}$	β_{thermal}	E_a	$t_{1/2}$
		$\text{kJ} \cdot \text{mol}^{-1}$	h		$\text{kJ} \cdot \text{mol}^{-1}$	h
SCEAzo2-p-10	0.71 ± 0.03	35 ± 2	0.4	0.90 ± 0.02	84 ± 2	0.4
SCEAzo2-c-10	0.83 ± 0.02	33 ± 2	0.4	0.89 ± 0.01	70 ± 2	0.5
SCEAzo4-p-10	0.76 ± 0.02	21 ± 4	0.7	0.89 ± 0.02	83 ± 2	1.1
SCEAzo4-c-10	0.77 ± 0.01	21 ± 2	1.1	0.82 ± 0.01	78 ± 1	2.3

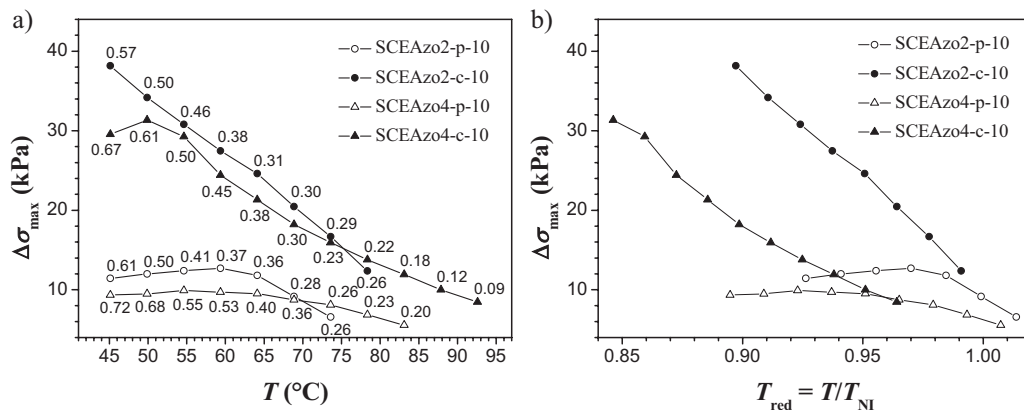


Figure 4. Maximum response ($\Delta\sigma_{\max}$) for all four SCLCEs a) as function of temperature, and b) as function of the reduced temperature. (Note: the values in the plot are the *cis*-isomer populations at the photo-stationary equilibrium).

response on bringing the polymer chains closer: the so-called cooperative effect.

The most important fact is that the responses of the samples are not showing a clear maximum in the vicinity of the clearing temperature, as predicted by the published literature.^[8] Only a pronounced decay as function of temperature was noticed for the elastomers with azobenzene crosslinkers, and a slight decay with a small local maximum in the case of the pendant groups. That can be explained by the *trans-cis* isomerization affecting T_{NI} but not the order. These azobenzene crosslinkers have a higher mechanical effect than the disorder generated by the *cis*-isomer in the LC matrix. Another relevant fact is that all samples are more efficient at low temperatures, where the Young's modulus is higher (see Supporting Information SI-5) when approaching T_g .^[24]

Photo-Isomerization and Thermal-Isomerization: Kinetics and Activation Energies

The fitting curves of each opto-mechanical experiment at different temperatures give the information about kinetics

of photo- and thermal-isomerization. In Figure 5, the normalized mechanical responses as function of time, under irradiation, and in the darkness, are shown. From these curves, the kinetic constants and *cis*-isomer populations can be determined using the values of the kinetic constants k_1 and k_2 , $\phi_{cis} = k_2/(k_1 + k_2)$ (see Supporting Information, Table SI-3). All single experiments are summarized in the Supporting Information (Table SI-1, SI-2 and SI-3) for the four photoactive SCLCEs at the different experimental temperatures.

It is a well-known fact that raising the temperature increases the reaction rate of both isomerizations. Quantitatively this relationship between the rate of a reaction and its temperature is determined by the Arrhenius equation $k = A \exp(-E_a/RT)$, where k is the kinetic constant, A the pre-exponential factor, E_a the activation energy, R the universal gas constant, and T is the temperature. From the Arrhenius curves for each sample (see Supporting Information, Figure SI-3), the activation energies of both processes were determined. In Table 1, the activation energies and half-life times are summarized for all photoactive LCEs.

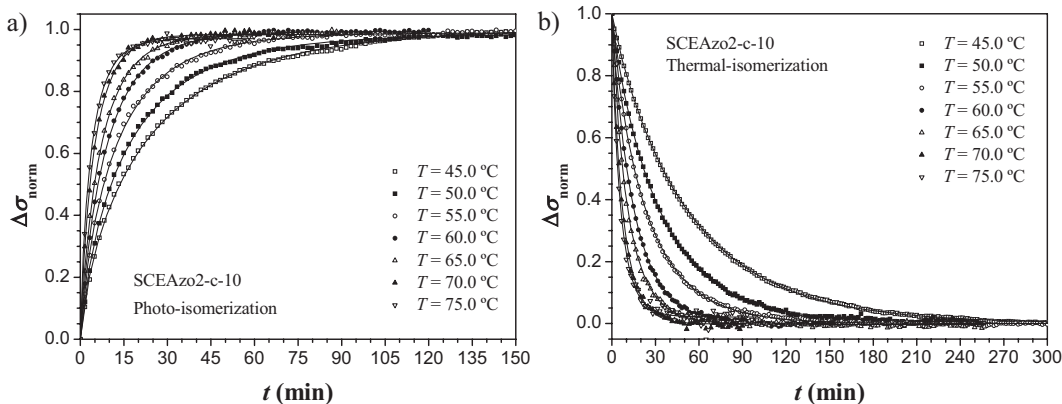


Figure 5. Normalized a) photo-isomerization curves and b) thermal-isomerization curves for the sample SCEAzo2-c-10 at different temperatures.

The activation energy in the photo-isomerization process depends on the nature of the azobenzene compound. In these side-chain systems, we can observe similar values for the two aromatic-ring azobenzene compounds (SCEAzo2-p-10 and SCEAzo2-c-10), about $35 \text{ kJ} \cdot \text{mol}^{-1}$, and similar energies for both four-member ring azobenzene compounds (SCEAzo4-p-10 and SCEAzo4-c-10), about $20 \text{ kJ} \cdot \text{mol}^{-1}$. In the thermal-isomerization process, the azobenzene crosslinkers have smaller energetic barriers ($75 \text{ kJ} \cdot \text{mol}^{-1}$), compared with the pendant groups ($85 \text{ kJ} \cdot \text{mol}^{-1}$). This is explained by the network helping to recover the original *trans*-state, making the back-isomerization easier. All these values are in agreement with the values obtained from the Eyring equation $k = k_B \cdot T/h \exp(-\Delta H^\ddagger/RT) \cdot \exp(\Delta S^\ddagger/R)$, where the activation enthalpy ($\Delta H^\ddagger > 0$, endothermic) and activation entropy ($\Delta S^\ddagger < 0$, order) values could be calculated for both transition states during the irradiation and thermal processes (see Supporting Information, Table SI-4). Thus, a more organized transition state (more negative entropy values) leads to lower enthalpy needs.

The values obtained for the four photoactive SCLCEs during both photo- and thermal-isomerization processes fall on the same curve as azoderivatives in different solvents and low molecular-mass LC.^[31] Thus, the results indicate that both isomerization processes follow the same behaviour or isokinetic relationship^[32] during the transformation from *trans*-to-*cis* and *cis*-to-*trans* isomers: the inversion mechanism (see Supporting Information, Figure SI-4).

Conclusion

The response of new photosensitive nematic elastomers using a new opto-mechanical set-up that avoids all thermal effects and allows the irradiation at specific wavelengths has been studied. The change in architecture of azobenzene molecules showed the most effective as actuator. Specifically, azobenzene crosslinkers are more efficient than the common pendant molecules, and two-ring azobenzene molecules have higher response than the corresponding four-ring molecules in SCLCEs.

Using this opto-mechanical set-up we were able to study the pure photo-isomerization and thermal-isomerization processes at different temperatures, and to measure the maximum response of these systems. The results show no maximum mechanical response in the vicinity of the clearing temperature. Only at low temperatures the mechanical response is maximal due to the high elastic modulus when close to the glass transition temperature.

By increasing the temperature, both photo- and thermal-isomerization processes are accelerated, and the photo-stationary equilibrium is poor in *cis*-molecules, which are

responsible for the mechanical response of the system. That means that by increasing temperature, the kinetic rate of the systems is accelerated, but less mechanical response is obtained. The evaluation of the energies involved in these isomerization steps shows that LCEs stabilize better the azobenzene compounds, and make the thermal-isomerization easier.

Finally, the energies involved during the photo- and thermal-isomerization were determined, and the values showed a low energy barrier for the *trans*-to-*cis* excited state compared to the *trans*-to-*cis* ground state. The mechanism involved for both processes is the same as for azobenzene molecules in LC solvents: the inversion mechanism.

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